AFOSR-TR-97-0392

REPORT DOCUMENTATION PAGE

17 SEP 1997

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE
August 31, 1997

3. REPORT TYPE AND DATES COVERED
Final July 1, 1994 - June 30, 1997

4. TITLE AND SUBTITLE
Beta-Alumina Fiber Matrix Interfacial Coatings

5. FUNDING NUMBERS
F49620-94-1-0375

6. AUTHOR(S) W.J. Lackey, J.S. Lewis, R. Richards, E. Pickering, H.C. King, M.A. Miller, G. Giannetti, B.N. Berkloff, L. Detter-Hoskin and B. Speer

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Georgia Institute of Technology
Atlanta, GA 30332-0405

8. PERFORMING ORGANIZATION REPORT NUMBER
E25-A22

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. Alexander Pechenik
Directorate of Aerospace and Materials Science
AFOSR.NI Bldg 410, Bolling Air Force Base
Washington, DC 20332-6448

N/A

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES COR:

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Three technical areas were pursued during this three year project: 1. oxidation resistant beta-alumina fiber-matrix interface coatings, 2. prediction and experimental verification of the microstructure of CVD/CVI carbon, and 3. a new class of laminated matrix composite. Magnetoplumbite and beta-alumina fiber coatings were synthesized by powder feeding of metalorganic reagents into a hot wall reactor. Annealing temperature was found to control both the phase assemblage and the extent of preferred orientation. For the second area, combination of thermodynamic-microstructure and densification models permitted prediction of the microstructure of the carbon matrix deposited during forced flow-thermal gradient chemical vapor infiltration (FCVI). The model also showed that it should be possible to deposit, by the FCVI process, either isotropic or highly anisotropic carbon. The former might be desirable for structural applications while the later is best when high thermal conductivity is of most interest. Finally, a new class of composite material possessing a laminated matrix was conceived. The new material was experimentally demonstrated with alternate layers of carbon and SiC having layer thicknesses in the range 0.01 to 0.5 μm. It is anticipated that the laminated matrix will enhance fracture toughness and may provide improved resistance to oxidation compared to carbo-carbon composites.

14. SUBJECT TERMS
Coatings, Chemical Vapor Deposition, CVD, Beta-Alumina, Carbon, Oxidation Protection, Fiber Coatings, Anisotropy

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18 298-102

Final Report
E25-A22

BETA-ALUMINA FIBER-MATRIX INTERFACIAL COATINGS

W. Jack Lackey, J.S. Lewis, R. Richards, E. Pickering, H.L. King, M.A. Miller, G. Giannetti, B.N. Beckloff, L. Detter-Hoskins and B. Speer

G. W. Woodruff School of Mechanical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0405

Prepared for
Dr. Alexander Pechenik
Air Force Office of Scientific Research
Washington, DC

Under Contract Number: F49620-94-1-0375

Final Report for the period July 1, 1994 to June 30, 1997

Beta-Alumina Fiber-Matrix Interfacial Coatings

Introduction

The initial objective of this three-year AASERT project was to develop an oxidation resistant beta-alumina or magnetoplumbite fiber-matrix interface coating that was resistant to oxidation. After about 18 months the goal, with the Program Manager's concurrence, was broadened to include other research still in the area of high temperature composites. As a result, a total of three technical areas were pursed. These were:

1. Beta-alumina and magnetoplumbite fiber-matrix interface coatings applied by CVD.
2. Development and experimental verification of a model for prediction of the anisotrospy in the carbon matrix of carbon-carbon composites prepared by forced flow-thermal gradient chemical vapor infiltration, and
3. Conception and demonstration of a new class of composites consisting of a reinforcement phase such as fiber or particulate and a matrix comprised of alternate thin layers of two or more materials. The remainder of this report is divided into those three areas.

Beta-Alumina Fiber-Matrix Interfacial Coatings

Excellent progress was made on this task. The majority of the work was performed by Ms. Regina Richards and co-op students Elliot Pickering, Harry King, and Michael Miller. Ms Richards' work culminated in her receiving an M.S. degree in Materials Science and Engineering. Her thesis "The Chemical Vapor Deposition of Hexagonal Aluminates As a Fiber-Matrix Interface Coating For Oxide-Oxide Composites", provides the details of her research and is available through the Georgia Tech library[1]. A brief summary follows:

Layered hexagonal aluminates with the beta-alumina and magnetoplumbite structure offer promise as oxidation resistant interface coatings for oxide-oxide composites. These structures consist of spinel-like blocks of Al^{3+} and O^{2-} ions with stabilizing cations in interstices between these layers. These blocks are bridged along the c-axis by Al-O-Al bonds that define weak basal planes that easily cleave. Possible extensive ion substitution produces the ideal formulae for β alumina and magnetoplumbite as $MAl_{11}O_{17}$ and $MAl_{11}O_{19}$, respectively, where M is a large cation.

Magnetoplumbite, $LaAl_{11}O_{18}$, and other aluminates were deposited by chemical vapor deposition (CVD) in hopes of achieving an oriented coating that would encourage debonding. The CVD process should favor the growth of hexagonal aluminates in the desired orientation, i.e., c-axis perpendicular to the substrate. The coatings were grown

on polycrystalline Al_2O_3 flat substrates and single-crystal Al_2O_3 fibers. A statistical study was conducted to optimize the coatings by varying the experimental CVD parameters. A four factor factorial with a central composite design (CCD) allowed for variation of deposition temperature, reagent powder input ratio, annealing temperature, and gas flow rates. The coatings were characterized with x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). Two software packages, Minitab 7.2 and Statgraphics 5.0, were used to perform statistical analyses on the characterization results of the sutdy.

XRD patterns showed that all the coatings were amorphous in the as-deposited state. Regression determined that the annealed coating phase assemblage was dependent on annealing temperature. A sharp phase transformation was seen from $LaAlO_3$ to $LaAl_{11}O_{18}$ at 1400°C. The higher the annealing temperature, the more likely the phase had completely transformed to $LaAl_{11}O_{18}$.

Stoichiometries produced by EDS did not correspond to phases present in the coatings. However, EDS analysis was used to model the compositional variation of the Al to La ratios in the coatings. Regression revealed that the Al to La ratio in the as-deposited coatings increased with increasing deposition temperature, indicating that the aluminum reagent deposited more efficiently than the lanthanum reagent at higher temperatures. The Al to La powder input ration also appeared to have a slight influence on the Al to La ratio in the as-deposited coatings. However, the regression equation generated for the Al to La ratio in the annealed coatings was a complex, empirical model that was difficult to physically describe. This seven factor surface response did reveal effects from annealing temperature and the interaction of deposition temperature and the Al to La powder input ratio.

SEM micrographs of surface morphology and fracture surface interfaces revealed that the desired c-axis orientation increased with annealing temperature. This was further verified on XRD patterns by the increase in basal plane peak intensities with increasing annealing temperature. There was concern that high temperature annealing would be detrimental to the strength of the substrates. However, cracks that propagated parallel to the substrate were observed in several coatings. Also, annealing did not appear to cause significant interaction between the substrate and coating. This lack of substrate-coating interaction lead to the theory that an extra Al_2O_3 phase was being deposited initially. This experimental work did offer a promising result in that a $LaAl_{11}O_{18}$ interface coating could have the ability to debond, thus possible toughening an oxide-oxide composite. However, the effectiveness of a $LaAl_{11}O_{18}$ interface coating seemed to depend more on the morphology and phase assemblage, which was controlled by annealing temperature, than on the compositional models produced by regression. The results of the statistical study proved that annealing temperature was the most important experimental parameter in the deposition of optimum $LaAl_{11}O_{18}$ coatings.

Model for Prediction of Carbon Matrix Microstructure

It is well known that the microstructure, that is, the degree of preferred orientation of the crystallites, of pyrolytic carbon is strongly dependent on the processing conditions and can vary from highly isotropic to highly anisotropic. Also, it is clear that the extent of the preferred orientation has a very large influence on mechanical, thermal, electrical, and other properties of CVD/CVI carbon. While the influence of processing conditions on the structure of CVD carbon is understood, the CVI of carbon is more complex and is not as thoroughly understood. That is, a model for prediction of the degree of anisotropy of CVI carbon is not available, primarily due to the complexities of knowing the gas phase chemistry as a function of position within the preform. In other words, the diffusional phenomena present in the conventional/diffusional types of CVI are difficult to analyze. The forced flow-thermal gradient CVI process (FCVI) is somewhat easier to analyze due to less reliance on diffusion, and a model for predicting the degree of anisotropy for a carbon matrix deposited via FCVI was developed and experimentally validated. The students participating in this effort were J.S. Lewis and S. Vaidyaraman. Mr. Lewis's work resulted in a B.S. thesis in the School of Materials Science and Engineering two open literature publications and a presentation.[2,3]. A condensed version of the paper won a Best Pater Award in the undergraduate student category. The model combined thermodynamics and the kinetics of densification of preforms with carbon via FCVI. The kinetic portion of the model is described in detail in Dr. Vaidyaraman's Ph.D. theses[4] and open literature publication[5]. Dr. Vaidyaraman's thesis placed second in the Carbon Journals international competition for Ph.D. theses in the area of carbon research. A brief summary of this work follows.

A model has been developed to predict the microstructure of the carbon matrix deposited during forced flow-thermal gradient chemical vapor infiltration (FCVI). This method employs previous thermodynamic-microstructure and densification models to determine conditions throughout the preform as a function of time. The model was verified by comparison with samples prepared over a range of deposition temperatures, reagent concentrations and flow rates. The model also showed that should be possible to deposit a matrix of uniformly high thermal conductivity onto conventional size carbon fibers, as well as small diameter, low cost, high thermal conductivity carbon whiskers.

Laminated Matrix Composites

A new class of composite materials referred to as "laminated matrix composites" was conceived and experimentally demonstrated. A patent application was filed with the U.S. Patent Office. The new material consists of fiber,particulate, or platelet reinforcement plus a laminated matrix. That is, the matrix consists of alternate thin layers of two or more materials. It is anticipated that both the reinforcement and the matrix will contribute to mechanical toughness. The research was performed by the following students from the School of Materials Science and Engineering here at Georgia Tech: John S. Lewis III, Harry C. King, Michael A. Miller, Giancardo Giannetti and Bruce N. Beckloff. Each of these students were able to perform their co-op work sessions with Dr. Lackey as a result of this AASERT project.

Three publications and two presentations, one of which was invited, have resulted from this research.[6-8]

A brief summary of this research follows.

A new type of composite, which consists of a reinforcement phase plus a matrix composed of many alternate thin layers of two different materials, has been prepared. CVI appears to be an appropriate process for the fabrication of this class of materials. We have successfully fabricated such a composite using the forced flow-thermal gradient CVI process. A carbon fibrous preform was infiltrated with alternate layers of C and SiC having thicknesses of 0.01 to 0.5μm. For a fixed cycle time, layer thicknesses increased with distance from the fiber surface. Crack deflection patterns indicate that the laminated matrix may contribute to mechanical toughness. More recently, we have replaced the fiber with SiC particulate and SiC platelets. Both were infiltrated with alternate layers of carbon and SiC. These reinforcements are considerably less expensive than fiber.

REFERENCES:

1. Regina Hardin Richards, "The Chemical Vapor Deposition of Hexagonal Aluminates As A Fiber-Matrix Interface Coating For Oxide-Oxide Composites", M.S. Thesis in Ceramic Engineering, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, February, 1995.

2. J.S. Lewis, W.J. Lackey, and S. Vaidyaraman, "Model for Prediction of Matrix Microstructure For Carbon/Carbon Composites Prepared by Forced Flow-Thermal Gradient CVI", Carbon 35 (1) 103-112, 1997.

3. W. J. Lackey, J.S. Lewis, and S. Vaidyaraman, "Model for Prediction of Matrix Microstructures for Carbon/Carbon Composites Prepared by CVI", Annual Meeting of the American Ceramic Society and Proceedings, Cincinnati, Ohio, May 4-7, 1997.

4. Sundararaman Vaidyaraman, "Carbon/Carbon Composites by Forced Flow-Thermal Gradient Chemical Vapor Infiltration (FCVI) Process," Ph.D. Thesis in the School of Chemical Engineering, Georgia Institutes of Technology, Atlanta, GA, September, 1995.

5. S. Vaidyaraman, W.J. Lackey, P.K. Agrawal, and T.L. Starr, "1-D Model for Forced Flow-Thermal Gradient Chemical Vapor Infiltration Process for Carbon", Carbon 34 (9) 1123-1133, 1996.

6. W. Jack Lackey, Sundar Vaidyaraman, and Karren L. More, "Laminated C-SiC Matrix Composites Produced by CVI," Journal American Ceramic Society 80 (1) 113-116, 1997.

7. W. J. Lackey, S. Vaidyaraman, and K.L. More, "Laminated Matrix Composites-A New Class of Materials", Ceramic Engineering Science Proceedings, 17 (4B) 166-173, 1996.

8. W. Jack Lackey, "H. C. King III, M.A. Miller, and K.L. More, "Laminated C-SiC Matrix composites Produced by CVI", Annual Meeting of The American Ceramic Society and Proceedings, Cincinnati, Ohio, May 4-7, 1997.